Pestic. Sci. 1996, **48**, 247–252

Phototransformation of Triadimefon on Glass and Soil Surfaces

Subir K. Nag* and Prem Dureja‡

Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi—110012, India

(Received 21 February 1996; revised version received 6 June 1996; accepted 2 July 1996)

Abstract: Photodegradation of triadimefon has been studied on glass and soil surfaces. A number of photoproducts have been isolated and characterised by NMR, IR and MS. Photolysis resulted in considerable amounts of 1-(4-chlorophenoxymethyl)-1,2,4-triazole, 1-(4-chlorophenoxy)-2,2-dimethyl-1-(1,2,4-triazol-1-yl)propane, 1-(1,2,4-triazol-1-yl)-3,3-dimethylbutan-2-one and 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-ol. Rates of photodegradation on glass and soil surfaces under UV and sunlight followed first-order kinetics with a significant correlation coefficient. Photodegradation was greater on alluvial soil than on laterite soil.

Key words: photodegradation, alluvial soil, laterite soil, UV and sunlight, triadimefon

1 INTRODUCTION

Triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1- (1*H*-1,2,4-triazol-1-yl)butan-2-one (Fig. 1, **1**) is a very good protectant and eradicant fungicide against powdery mildew and rust fungi.[1] It has been claimed to move systemically after application to roots or leaves of cereals[2] and basipetally in cucumber and barley.[3] Its activity is probably enhanced as a result of considerable redistribution in the vapour phase. It is also used as a foliage fungicide[4] and as a soil fungicide.[5,6] Triadimefon is metabolised by different fungal species,[7] in higher plants[8] and in soil,[7] mainly to triadimenol (as a result of reduction of the carbonyl to a hydroxy group) and 4-chlorophenol. Photolysis of triadimefon in methanol in a borosilicate glass apparatus using a medium pressure mercury vapour lamp (400 W) gave 1,2,4-triazole, 4-chlorophenol, 4-chlorophenylmethyl carbonate and an unidentified product (mol. wt. 175).[7] The present paper deals with the rate of photolysis and nature of different photoproducts of triadimefon formed as a thin film on a glass surface and on a soil surface under sunlight and ultra-violet light.

* Present address: Scientist, Division of Plant Protection, Indian Grassland and Fodder Research Institute (IGFRI), Jhansi-284003, UP, India.
‡ To whom correspondence should be addressed.

2 MATERIALS AND METHODS

2.1 Materials

A technical sample of triadimefon (95%) was supplied by Bayer (India) Ltd. It was purified further by repeated crystallisation from benzene and hexane to constant melting point, 80–81°C, and shown to be chromatographically pure (TLC and GLC). The solvents used were of analytical grade.

2.2 Soil characteristics

Two types of soil, alluvial and laterite, were used in the experiment. Their properties are given in Table 1.

2.3 Chromatography

Triadimefon degradation rates were determined using a Hewlett Packard Model 5890 series II Gas Liquid Chromatograph equipped with an electron capture detector and a capillary column (HP-1, methyl silicone gum, 10 m × 0·53 mm ID × 2·63 μm film thickness) coupled with a Hewlett Packard 3390A integrator. The oven, injector and detector temperatures were 160°C, 250°C and 300°C respectively. Nitrogen, at

Pestic. Sci. 0031-613X/96/$09.00

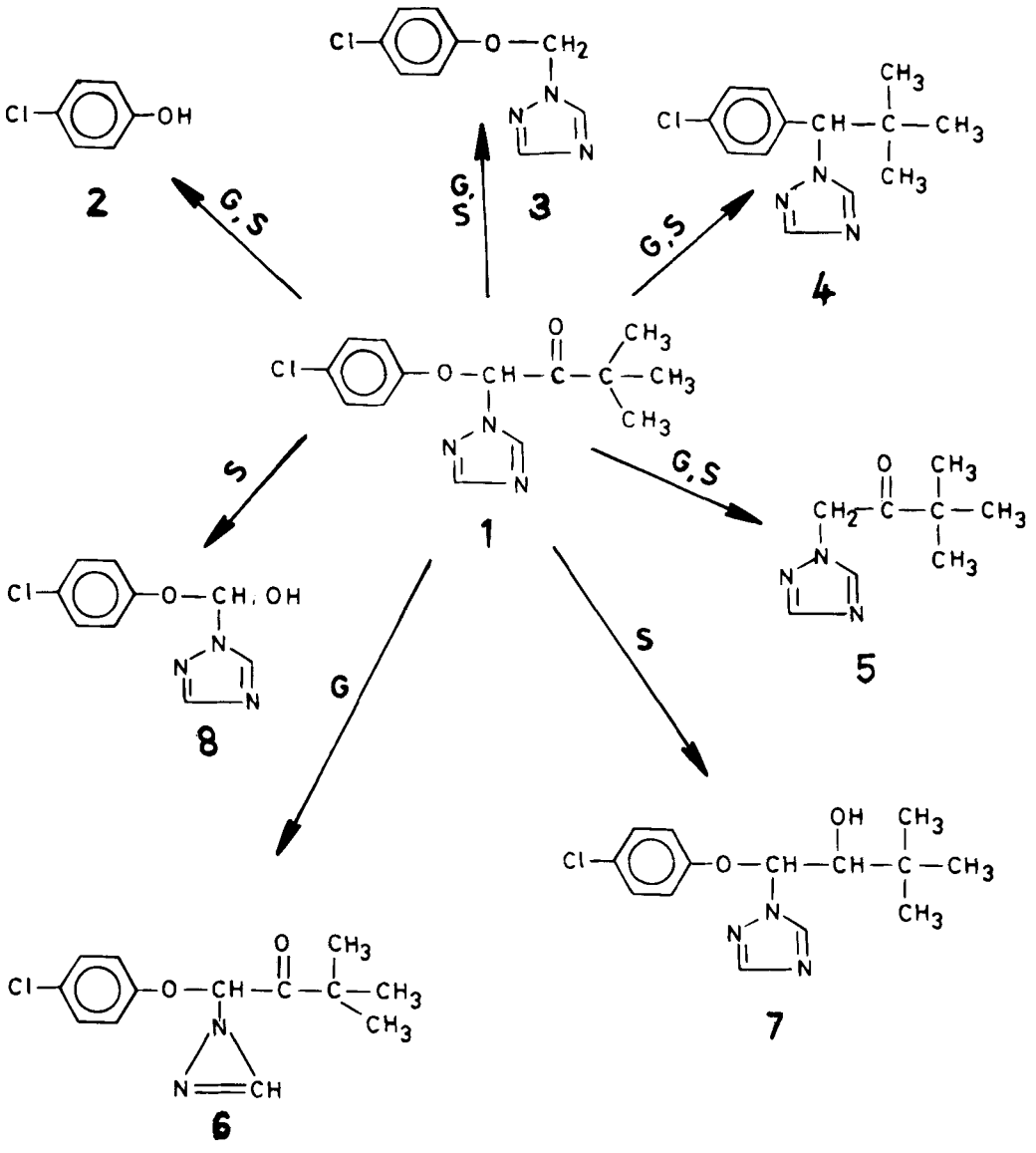

Fig. 1. Possible photoproducts of triadimefon on glass (G) and soil (S) surface.

20 ml min^{-1} was used as carrier gas. TLC was performed on 20 × 20 cm glass plates coated with silica-gel G (0·5 mm). The mobile phases used for TLC were hexane + acetone (4 + 1 by volume) and hexane + diethyl ether + formic acid (20 + 19 + 1 by volume), with iodine as the chromogenic reagent. Photoproducts were separated by column chromatography using a glass column (75 cm × 2 cm ID) containing 500 g of 60–100 mesh preactivated silica gel in hexane.

2.4 Spectrometric analysis

The ultraviolet-visible (UV-VIS) spectrum of triadimefon in methanol was recorded on a Hitachi Model

TABLE 1
Physicochemical Properties of Soils Used in This Work

Soil type	*Soil order*	*pH*	*Organic carbon* (%)	*Clay* (%)	*CEC* (*Cmol* kg^{-1})
Alluvial	Inceptisol	7·4	0·47	12·75	15·1
Laterite	Alfisol	5·3	0·22	22·20	10·9

V-2000 double beam UV-VIS spectrophotometer using a quartz cuvette (1 cm path length). The infrared (IR) spectra of products were recorded on a Nicolet Impact-700 FT-IR spectrophotometer. [^{1}H] NMR spectra were recorded on a Varian EM 360L (60 MHz) instrument. Deuterochloroform ($CDCl_3$) or carbon tetrachloride (CCl_4) was used as solvent and tetramethylsilane (TMS) as the internal standard for NMR. GC–MS studies involved a HRGC-MEGA 2 series gas chromatograph coupled to a Fisons-Trio 1000 ion trap mass spectrometer. The ionisation potential was 70 eV. The gas chromatograph was equipped with a SE-54 capillary column (15 m × 0·25 mm, ID, film thickness 0·1–0·15 μm). The conditions were as follows: initial temperature 60°C for 1 min and then raised (15°C min^{-1}) to 250°C and held for 10 min. Helium was used as the carrier gas.

2.5 Photolysis equipment and photolysis procedure

2.5.1 Photolysis on glass surface as thin film

For studies on a glass surface, a solution of triadimefon in acetone (10 ml, 1 mg ml^{-1}) was applied uniformly to the inner surface of glass Petri plates (20 cm dia.) with a pipette. The solvent was evaporated at room temperature, leaving behind a thin layer of triadimefon. These plates were exposed to UV light by placing them under an ultra-violet lamp at a distance of 30 cm (the light produced by these lamps was rich in irradiation at 254 nm, and temperature varied at the test surface between 25 and 30°C) and irradiated for 4 h, after which each plate was extracted with acetone (5 × 4 ml). The combined extracts were concentrated and photoproducts were separated by column chromatography, eluting with hexane and hexane + acetone in different ratios. A set of Petri plates were also exposed to sunlight in the month of September between 9 a.m. and 5 p.m. (8 h day^{-1}) for 48 h, on an area of a roof protected as much as possible from wind and rain by covering them with quartz glass. Sunlight intensity at wavelengths between 300 and 400 nm was approximately 720, 780 and 350 mW cm^{-2} at the beginning, middle and end of the day respectively. The temperature varied at the test surface between 30 and 35°C. Compounds were identified by GC-MS using authentic standards for comparison.

2.5.2 Photolysis on soil surface

Sieved alluvial soil (2 mm; 50 g) was slurried with double-distilled water and sprayed uniformly onto Petri plates (20 cm diam.) to give a layer 2 mm thick which was air-dried. Triadimefon in acetone (10 ml, 1 mg ml^{-1}) was applied uniformly to the surface of the soil using a pipette. The plates were again air-dried and then irradiated under UV light (254 nm) for 48 h or sunlight for 15 days. After irradiation, the soil was removed and extracted with acetone (5 × 4 ml), the acetone extracts from several plates being combined and concentrated at low temperature. Photoproducts were identified by GC-MS using authentic standards for comparison.

2.5.3 Rate of photodegradation of triadimefon on glass surface

Triadimefon in acetone (10 mg litre^{-1}; 1 ml) was applied uniformly to Petri plates (5 cm diam.) using a pipette, and the solvent allowed to evaporate. The plates were then exposed to UV light (254 nm) for 8 h or sunlight (average 7–8 h day^{-1}) for 24 h during the month of September 1994. One set of plates were covered with aluminium foil and kept in the dark as control. Sample plates were removed at intervals and extracted with acetone (5 × 3 ml). The volume of the combined extract was reduced to 1 ml and this solution was used for GLC analyses.

2.5.4 Rate of photodegradation of triadimefon on soil surface

The rate of photodegradation of triadimefon was studied on alluvial and laterite soil. Soil passed through a 2-mm sieve was suspended in distilled water (1 g in 2 ml) and the suspension used to prepare a thin layer on the bottom of a Petri plate (5 cm diam.). Air-drying resulted in a thin uniform layer of soil on the glass surface. A solution of triadimefon in acetone (10 mg litre^{-1}; 1 ml) was added and the solvent allowed to evaporate at room temperature. The plates were exposed to UV light for 36 h or sunlight for 30 days and three sample plates removed at given time intervals. Plates covered with aluminium foil and kept in the dark served as controls. After irradiation, soil was scraped from each plate and extracted with acetone (5 × 4 ml) and the combined extract was then centrifuged (3000 rev min^{-1}; 20 min). The supernatant was concentrated to 1 ml and used for GLC analyses.

2.6 Synthesis

2.6.1 Preparation of authentic compounds for comparison

Pinacol hydrate and pinacolone were synthesised by the procedure as described by Vogel.[9]

2.6.2 1-Bromo-3,3-dimethyl-2-butanone

Bromine (5 ml) dissolved in glacial acetic acid (10 ml) was added dropwise to a solution of pinacolone (10 g) in acetic acid (10 ml) with constant stirring, maintaining the temperature at 25°C and the solution then stirred for a further 2 h. The resulting solution was extracted with hexane, the hexane extract dried over sodium sulfate and the solvent removed. The residue was distilled at 71°C and 10 mm Hg pressure, giving a product whose infrared spectrum showed a peak at 1715 cm^{-1}

corresponding to a C = O group. [^{1}H] NMR (CCl_4) δ: 4·1 (s, 2H, CH_3), 1·3 (s, 9H, $C(CH_3)_3$).

2.6.3 1-(4-Chlorophenoxy)-3,3-dimethyl-butan-2-one

A solution of 1-bromopinacolone (100 mg) and 4-chlorophenol (300 mg) in dry benzene (10 ml) was refluxed in the presence of anhydrous potassium carbonate (1 g) for 4 h. The solution was filtered to remove potassium carbonate and the benzene layer separated and extracted with sodium hydroxide solution (100 g litre^{-1}) to remove unreacted chlorophenol, then washed several times with after. The benzene layer was dried over anhydrous sodium sulfate and the solvent removed, leaving a yellow oil which solidified on standing (mp. 63–65°C). It was purified by column chromatography. A peak at 1728 cm^{-1} in the IR spectrum of the product indicated the presence of a carbonyl group. [^{1}H] NMR ($CDCl_3$) δ: 7·2 (d, 2H, J = 6 Hz, aromatic), 6·8 (d, 2H, J = 7 Hz, aromatic), 4·6 (s, 2H, CH_3), 1·1 [s, 9H, $C(CH_3)_3$]. This compound was reported in 1986 by Clark and Watkins.[10]

2.6.4 1-(1,2,4-Triazol-1yl)-3,3-dimethyl-2-butanone

A solution of 1,2,4-triazole (200 mg) and 1-bromopinacolone (600 mg) in dry acetone was refluxed for 4 h in presence of anhydrous potassium carbonate (1 g). The solution was filtered to remove potassium carbonate and the filtrate was evaporated to dryness. The residue, subjected to column chromatography, gave a solid which was crystalliised from methanol to give a colourless amorphous solid, the IR spectrum of which had a peak at 1731 cm^{-1}, indicating a carbonyl group. [^{1}H] NMR ($CDCl_3$) δ: 8·2 (s, 1H), 7·9 (s, 1H), 5·3 (s, 2H, CH_3) and 1·2 [s, 9H, $C(CH_3)_3$].

3 RESULTS AND DISCUSSION

3.1 Photolysis on glass surface as thin film under UV light

Column chromatography of the extract from the photolysis experiment gave on elution with hexane + acetone (98 + 2 by volume) a colourless liquid, which solidified on cooling and had m.p. 43°C.

The [^{1}H] NMR spectrum of this product ($CDCl_3$) showed the presence of four aromatic protons at δ 7·8. Its mass spectrum showed the molecular ion peak at *m/z* 128/130 with fragment ion peaks at *m/z* 93 (M^+-Cl). It was identified as 4-chlorophenol (**2**; Fig. 1). The [^{1}H] NMR spectrum of another eluate showed the presence of two triazole protons at δ 8·3 and 8·0, four aromatic protons at δ 7·4 and 7·2 and a benzylic proton at δ 6·0. Its mass spectrum showed molecular ion peak at *m/z* 209 with fragment ion peaks at *m/z* 179 and *m/z* 128. The [^{1}H] NMR spectrum did not indicate the presence of *tert*-butyl protons. This product (**3**; Fig. 1) was characterised as 1-(4-chlorophenoxymethyl)-1,2,4-triazole.

Further elution of the column with hexane + acetone (97 + 3 by volume) gave a liquid which was further purified by preparative TLC. The [^{1}H] NMR spectrum of this photoproduct showed the presence of triazole, aromatic ring and *tert*-butyl protons, but the IR spectrum did not indicate the presence of a carbonyl group. MS gave a molecular ion peak at *m/z* 265. On the basis of the spectroscopic evidence, this compound was identified as 1-(4-chlorophenoxy)-2,2-dimethyl-1-(1,2,4-triazol-1-yl)propane (**4**; Fig. 1).

Further elution of the column using hexane + acetone (96 + 4 by volume) gave a solid which, when recrystallised from methanol, gave a colourless amorphous solid with [^{1}H] NMR ($CDCl_3$) δ: 8·2 (s, 1H), 7·9 (s, 1H), 5·3 (s, 2H), 1·2 (s, 9H); MS: 167, 112, 83, 70, 57 and IR (V_{max}, KBr): 3432 cm^{-1}, 3127 cm^{-1}, 1731 cm^{-1}.

The comparison of the NMR, MS and IR data with those of an authentic specimen identified this compound as 1-(1,2,4-triazol-1-yl)-3,3-dimethyl-butan-2-one (**5**; Fig. 1).

Increasing the acetone component of the eluate to 95 + 5 by volume gave a liquid which was further purified by preparative TLC. Since only a small amount of this product was obtained, it was identified on the basis of mass spectrum which showed the molecular ion peak at *m/z* 267/269 (MH^+) with fragment ion peaks at *m/z* 209 (M^+-57), *m/z* 181 (M^+-85), *m/z* 128 (ClC_6H_4OH) and at *m/z* 111/113 (ClC_6H_4), consistent with 1-(4-chlorophenoxy)-(1-diazirin-1-yl-3,3-dimethyl-butan-2-one (**6**; Fig. 1).

3.2 Photolysis on glass surface under sunlight

Compounds **2**, **3**, **4** and **5** were identified after sunlight irradiation by GC-MS using authentic standards for comparison. The rate of formation of these photoproducts was slow under sunlight in comparison to UV light.

3.3 Photolysis on a soil surface under UV light

The photolytic degradation of triadimefon was studied on alluvial soil under UV light. The residue from the extract of irradiated soil was analysed by GC-MS. The molecular ion peaks at *m/z* 128/130 (M^+), *m/z* 209 (M^+), *m/z* 265/267 (M^+) and 167 (M^+) indicated the presence of compounds **2**–**5** (Fig. 1) which were obtained by irradiation of triadimefon on a glass surface. Two other compounds (**7** and **8**) were also present and were tentatively identified by GC-MS.

The mass spectrum of the compound **7** had (M^+) at *m/z* 295 (M^+) with fragment ion peaks at *m/z* 260 (M^+-

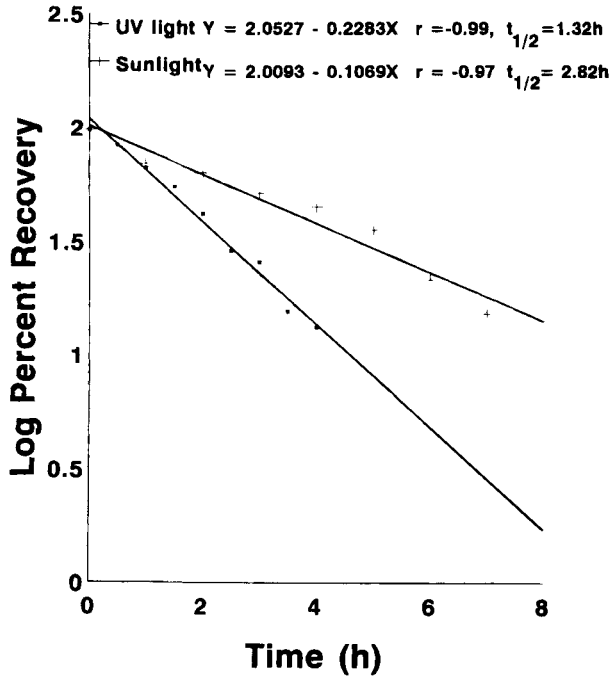

Fig. 2. Linear plot for first-order kinetics of loss of triadimefon from thin film on glass surface.

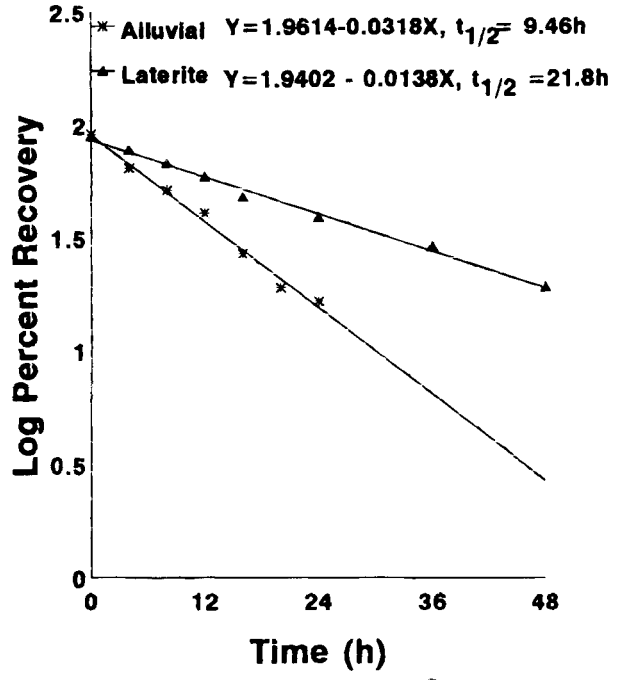

Fig. 3. Linear plot for first-order kinetics of loss of triadimefon from soil surface under UV light.

35) due to loss of chlorine atom from the molecule, *m/z* 208 (M^+-87), *m/z* 128, *m/z* 69 and *m/z* 57. The mass fragment at *m/z* 128 indicated the presence of a 4-chlorophenol moiety in the compound, and it was identified as 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-ol, the well-known fungicide triadimenol (**7**; Fig. 1).

The MS analysis of compound **8** showed (M^+) at *m/z* 224 with fragment ion peaks at *m/z* 208/210, *m/z* 181/183, *m/z* 140, *m/z* 127/128 and *m/z* 111/113 which identified it as 4-chlorophenoxy-(1,2,4-triazol-1-yl)methanol (**8**; Fig. 1).

3.4 Photolysis on a soil surface under sunlight

Compounds **2**, **3**, **4** and **7** were detected on a soil surface after sunlight irradiation, using GC-MS and authentic standards for comparison.

The rate and distribution of the products shown in Fig. 1 depend upon the phase in which photolysis is being carried out. Products **3**, **4** and **5** occur as major and **2** and **6** as minor components of the degradation mixture on a glass surface, whereas **3**, **4**, **5** and **7** are major and **2** and **8** are minor products of degradation on a soil surface under UV light. Products **2**, **3** and **5** occur as major components and **4** as a minor component of the degradation mixture on a glass surface, and **2**, **3** and **7** are major products and **4** a minor product on a soil surface under sunlight. The products are formed as a result of breaking of the bond between phenolic oxygen and C-1 carbon and cleavage of C-1 and C-2 carbon atoms.[7] The formation of compound **4** in large concentration under UV light suggested that a concerted process involving simultaneous combination and loss of C = O might be involved, rather than simple coupling of the discrete free radicals after loss of C = O from triadimefon.

TABLE 2
Rate Constant and Half-Life Values for Triadimefon on Different Soils and Glass Surface under UV and Sunlight

Soil type	*Light used*	*Rate constant, k*	*Half life*[a]	r^2
Alluvial	UV	0·0732 h^{-1}	9·46 h	0·99
Laterite	UV	0·0317 h^{-1}	21·80 h	0·99
Alluvial	Sunlight	0·0430 day^{-1}	16·09 d	0·99
Laterite	Sunlight	0·0426 day^{-1}	18·24 d	0·97
Glass surface	UV	0·5258 h^{-1}	1·32 h	0·98
Glass surface	Sunlight	0·2462 h^{-1}	2·82 h	0·94

[a] Mean of three replicates.

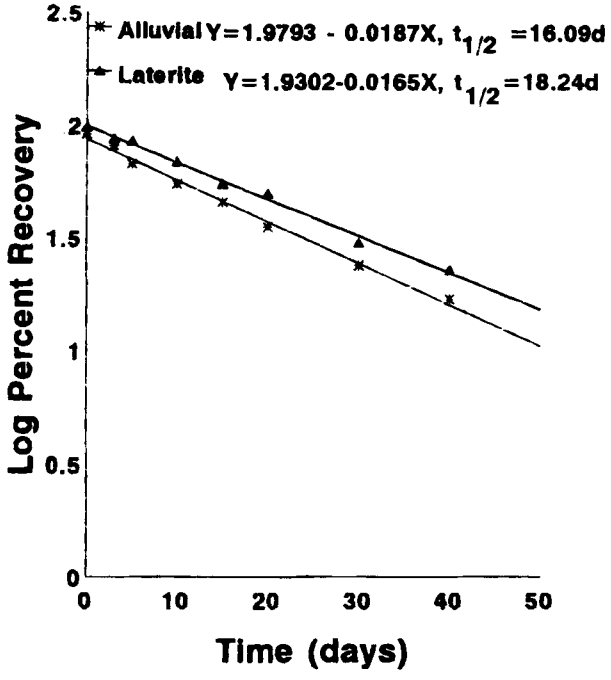

Fig. 4. Linear plot for first-order kinetics of loss of triadimefon from soil surface under sunlight.

3.5 Rate of degradation of triadimefon

The rate of photodegradation of triadimefon was studied on a glass surface, and on alluvial and laterite soil under UV light as well as under sunlight. Virtually no degradation of triadimefon occurred in the dark since 90% of the applied triadimefon was recovered unchanged after 48 h under UV light or 30 days under sunlight. This indicates that triadimefon is stable under these conditions and the time frame of this study and the degradation observed in this study can be attributed to photolysis only. The rate of degradation followed first-order kinetics with significant correlation coefficient (Figs 2, 3 and 4). The rate constant and half life values of triadimefon on different soils and on a glass surface under UV light and sunlight are given in Table 2. The rate of degradation was greater on glass than on soil surfaces. This may be due to the fact that some pesticides are adsorbed on soil clays and other colloidal substances and so become less available to light. The rate of degradation is higher on alluvial soil than on laterite soil under both UV light and sunlight (Table 2). This may be due to the difference in organic content and pH of the soil (Table 1).

4 CONCLUSION

These studies indicate that under the influence of light, triadimefon undergoes cleavage of the C-1 to C-2 bond, C-1 to triazole bond, hydrolysis, reduction[7] and extrusion of C = O. Since most of these photoproducts have been detected on both soil and glass surfaces under both UV as well as sunlight, it is presumed that they are likely to be present as residues on treated crops.[10]

ACKNOWLEDGEMENTS

We thank Dr S. K. Handa, Head of the Division of Agricultural Chemicals, for providing facilities for carrying out the work.

REFERENCES

1. Buchenauer, H., Studies on the systemic activity of Bayleton (Triadimefon) and its effect against certain fungal diseases of cereals. *Pflanzenschutz-Nachrichten Bayer*, **29** (1976) 266–80.
2. Frohberger, P. E. New approaches to the control of cereal diseases with triadimefon (MEB 6447). *VIII Int. Plant Protection Congress*, Moscow (1975), Reports and Information, Section III, Part 1, 247–58.
3. Scheinpflug, H. & Paul, V. On the mode of action of Triadimefon. *Neth. J. Plant Pathol.*, **83** (1977) 105–11.
4. Wright, F. E., Verser, J. W. & Gipson, R. D., Selective control of various foliar pathogens in wheat using fungicides. *Phytopathology*, **73** (1983) 802.
5. Hardison, J. R. Control of *Puccinia striiformis* by two new systemic fungicides, BAY MEB 6447 and BAS 31702. *Plant Dis. Reptr*, **59** (1975) 652–5.
6. Hardison, J. R. Control of stripe and flag smut in Kentucky blue grass by a new systemic fungicide BAY MEB 6447. *Crop Sci.*, **14** (1976) 769.
7. Clark, T., Clifford, D. R., Deas, A. H. B., Gendle, P. & Watkins, D. A. M., Photolysis, metabolism and other factors influencing the performance of triadimefon as a powdery mildew fungicide. *Pestic. Sci.*, **9** (1978) 497–506.
8. Gasztonyl, M. & Josepovits, G., Translocation and metabolism of triadimefon in different plant species. *Acta Phytopathol. Acad. Sci. Hung.*, **13** (1978) 403–15.
9. Vogel, A. I., *Textbook of Practical Organic Chemistry*. ELBS/Longman, 5th edn, 1989, pp. 527–8.
10. Clark, T. & Watkins, D. A. M., Photolysis of triadimenol. *Chemosphere*, **15** (1986) 765–70.